Measuring Bond Angle Distributions in Silicate Glasses with 2D J PIETA NMR

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Introduction

The importance of measuring the distribution of Si-O-Si angles in silicate glasses cannot be overstated. It is the first broken structural constraint and the variation in these angles is considered to be one of the main sources of disorder in silicate glasses. The $^2J_{Si\text{-}O\text{-}Si}$ coupling in nuclear magnetic resonance (NMR) spectroscopy can be used as a probe of structure in the Si-O-Si linkage, although the size of this coupling in silicates is on the order of 0 to 15 Hz. The greatest utility of the $^2J_{Si\text{-}O\text{-}Si}$ coupling, to date, has been in establishing through-bond connectivities between $Q^{(n)}$ units, forming the basis of a number of successful INADEQUATE NMR studies in silicates, as well as analogous ^{31}P NMR studies exploiting the $^2J_{P\text{-}O\text{-}P}$ coupling in phosphate glasses.

We recently developed the Phase Incremented Echo Train Acquisition (PIETA) method for more accurate measurement of transverse relaxation behavior and J coupling evolution during echo train acquisition. In this three-dimensional experiment we separate and correlate the ^{29}Si chemical shift to the ^{29}Si-^{29}Si J coupling spectrum to the ^{29}Si T_2 relaxation "spectrum". Our results on silica glass show a Si-O-Si bond angle distribution that is similar to previous ^{17}O DAS NMR results with a distribution peak at 147◦ and extending over a range of angles from 140◦ to 154◦. We will also present results on mesoporous silica with 4 nm ordered pores. Here the bond angle distribution peaks at 146◦ and extending over a range of angles from 140◦ to 153◦. Interestingly, we observe little variation in the distribution of $^2J_{Si\text{-}O\text{-}Si}$ couplings for the $Q^{(3)}$ site, consistent with the $Q^{(3)}$ residing on the walls of the ordered pores.

Structure of Inorganic Oxide Glasses: What's Ordered? What's Disordered?

Atomic Arrangement in Two-Dimensional Silica:
From Crystalline to Vitreous Structures
L. Lichtenstein, M. Heyde, and H.-J. Freund, J. Phys. Chem. C 2012, 116, 20426−20432

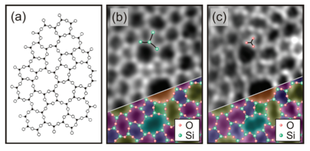


Figure 1. (a) Zachariasen's scheme of a random network (black dots: cations, white circles: anions). (b, c) Both images represent a single atomically resolved constant height measurement, where panel b shows the nc-AFM and panel c the STM channel. Imaging parameters for b: oscillation amplitude = 0.27 nm, gray scale from −1.0 Hz (dark) to +0.6 Hz (bright); for c: V_S = 100 mV, gray scale from 50 pA (dark) to 500 pA (bright); for both b and c: scan area = 2.7 nm × 3.9 nm. In panel b the structure of the Si atoms is visible, whereas panel c reveals the arrangement of the O atoms. An atomic model of the topmost layer of the silica film is superimposed onto the lower right corner of the images in panels b and c (green balls: Si atoms, red balls: O atoms).

Nanostructure and atomic structure of glass seen by atomic force microscopy
G.H. Frischat, J.-F. Poggemann, G. Heide
J. Non-Cryst. Solids, 345&246, 197 (2004)

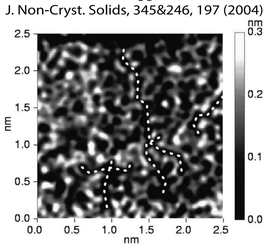
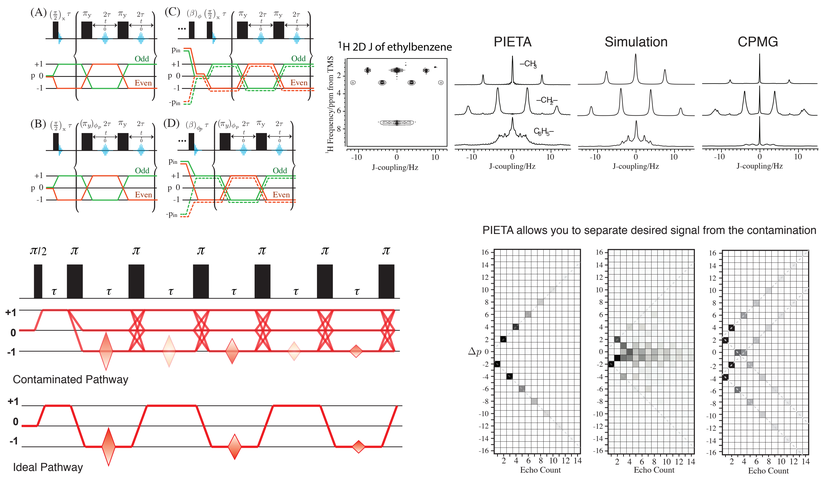
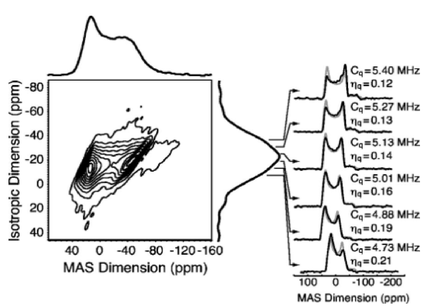


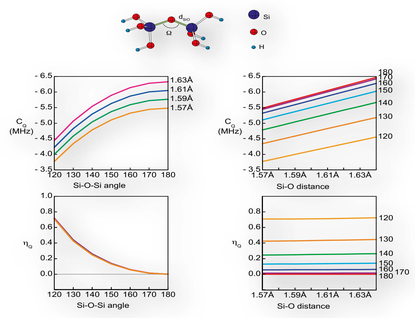
Fig. 7. Non-contact UHV-AFM image of an Na_2O-SiO_2 glass fracture surface, prepared at 1×10^{-11}mbar and imaged at 1×10^{-9}mbar. The dotted lines are guides to the eye to show some of the pathways.

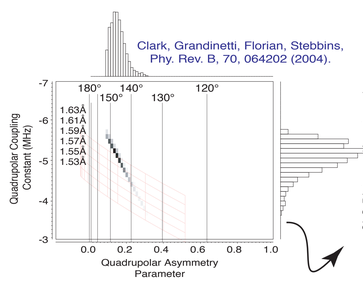
PIETA (Phase Incremented Echo Train Acquisition)

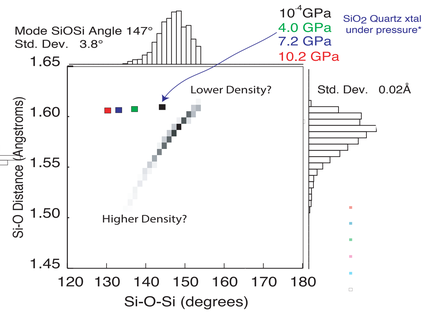


Si-O-Si Bond Angle Distributions in Silica Glass from ^{17}O NMR



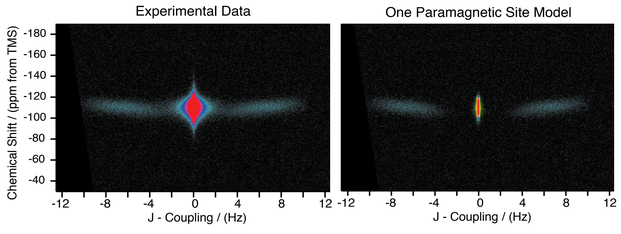


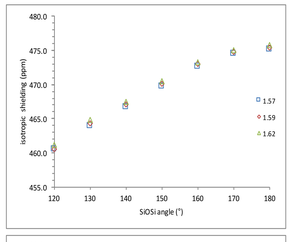


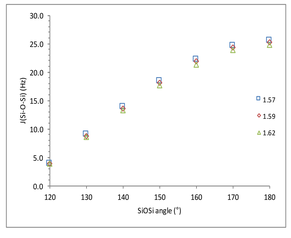


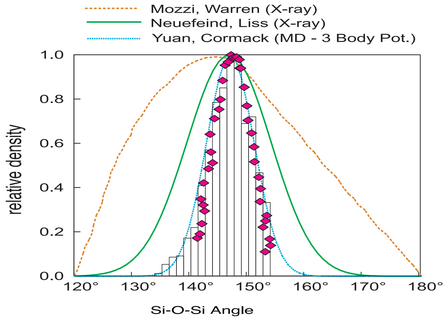
Si-O-Si Bond Angle Distributions in Silica Glass from ^{29}Si NMR

Silica SiO2 doped with paramagnetic CoO

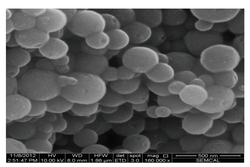


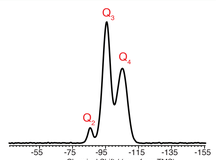






Si-O-Si Bond Angle Distributions in Mesoporous Silica from ^{29}Si NMR



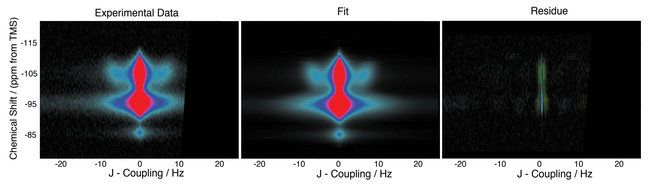


- 4 nm pore diameter with 200 nm particle sizes.

- The pore walls mainly comprise of $Q^{(3)}$ and $Q^{(2)}$ ^{29}Si sites.

- The pore walls are decorated with hydroxyl groups and pores filled with H_2O molecules.

- The core mainly comprises of $Q^{(4)}$ ^{29}Si sites.

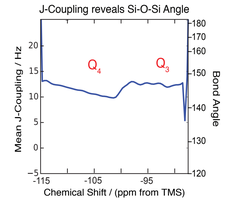


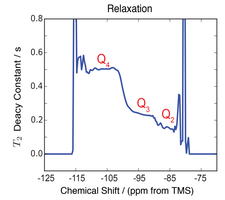
- J-Coupling distribution at $Q^{(4)}$ site show a distribution of bond angles, representing a disordered core.

- J-Coupling distribution at $Q^{(3)}$ site show little to no variation showing narrow range of bond angles. This is consistent with the fact that the pore walls are engineered to maintan an average pore size of 4 nm.

- The relaxation data show that the relaxation is mediated via the pores where the $Q^{(3)}$ and the $Q^{(2)}$ site relax faster than that of the $Q^{(4)}$ site.

- The relaxing agent is believed to be the dissolved paramagnetic O_2 in water.





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